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Ultrafast Spectroscopy of Arylchlorodiazirines: Hammett Correlations of Excited State Lifetimes

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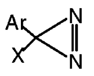
Arylhalocarbenes (ArCX), photochemically generated from arylhalodiazirines (**1**), have been central to absolute kinetics studies of carbene−alkene addition reactions.[1] Ultrafast laser flash photolysis (LFP) of **1** (X = F, Cl, Br) in acetonitrile (ACN) or cyclohexane (CHX) gave transients with $\lambda_{max} \approx 600-700$ nm and ps lifetimes that were assigned to excited state arylhalodiazirine precursors of ArCX.[2] Due to the dependence of the excited state lifetimes on solvent polarity and the electron-donating capacity of X, the excited states were depicted as diradicals/zwitterions **2**.[2,3] Now we present computational and ultrafast spectroscopic studies of phenylchlorodiazirine and five ring-substituted analogues (**3**) that permit a more precise representation of their excited states, as well as correlations of the excited state lifetimes with solvent polarity and the electronic properties of their aryl substituents.



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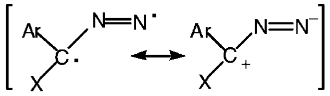

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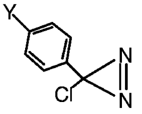

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Ultrafast LFP ($\lambda_{ex} = 375$ nm) of **3** (Y = H) in ACN affords a broadly absorbing transient with $\lambda_{max} = 625$ nm (Figure 1) within the 300 fs laser pulse.[4] The transient decays biexponentially with $\tau_1 = 2.8 \pm 0.3$ ps and $\tau_2 = 61.6 \pm 7.4$ ps (cf. Figure S-1 in the Supporting Information). In keeping with our previous report,[2] we assign this transient to an excited state of **3** (Y = H) and suggest that τ_1 represents intramolecular vibrational relaxation (IVR) of **3***.[5] We do not assign the 625 nm transient to singlet carbene PhCCl, notwithstanding that the carbene has a weak absorption in the 700 nm region,[6] because PhCCl (and ArCCl in general) decays much more slowly ($\tau \approx 0.1-10$ μs)[1] than the transient of Figure 1.

RI-CC2/TZVP and TD B3LYP/6-311+G(d,p) calculations predict the $S_0 \rightarrow S_1$ vertical transition of **3** (Y = H) at 342 or 401 nm, respectively,[7a] so that with λ_{max} of S_0 measured at 369 nm and λ_{ex} = 375 nm, we are confident that we are observing the S_1 state of **3**. The RI-CC2 computational method has reliably reproduced other electronic transitions.[7b] Similar transients are observed in $CHCl_3$ ($\tau_2 = 46.2 \pm 5.9$ ps) and in CHX ($\tau_2 = 13.3 \pm 3.1$ ps) and are also attributed to S_1 of **3** (Y = H); cf. Figures S-2 and S-3 in the Supporting Information.

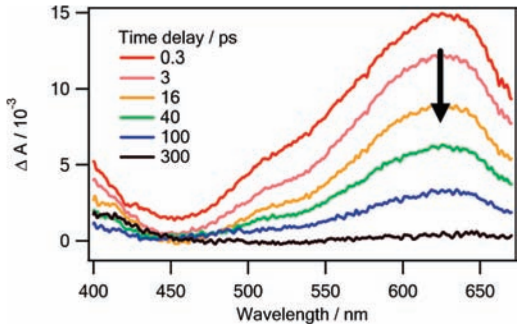

Figure 1. Transient spectra of **3*** (Y = H) in ACN generated by ultrafast LFP ($\lambda_{ex} = 375$ nm) with time windows of 0.3−300 ps.

Table 1. Lifetimes of Transient Absorptions of Arylchlorocarbenes[a]

Y in **3**	σ_p^{+b}	τ_{ACN}	τ_{CHCl3}	τ_{CHX}
p-MeO	−0.78	760 ± 22	644 ± 78	132 ± 12
p-CH_3	−0.31	150 ± 8.1	114 ± 8.3	25.8 ± 1.6
p-H	0.00	61.6 ± 7.4	46.2 ± 5.9	13.3 ± 3.1
p-Cl	0.11	50.0 ± 5.9	40.6 ± 8.1	8.0 ± 0.8
m-Cl	0.37	22.1 ± 2.9	16.5 ± 4.0	4.7 ± 0.2
p-CF_3	0.53[c]	10.6 ± 0.7	6.9 ± 0.8	2.5 ± 0.2

[a] In ps; only the long components of the transients' decays are tabulated. [b] σ_p^+ values are from March, J. *Advanced Organic Chemistry*, 4th ed.; New York: Wiley, 1992; p 280. [c] σ_p^+ is taken as identical to σ_P.

Five additional arylchlorodiazirines **3**, with Y = *p*-MeO, *p*-Me, *p*-Cl, *m*-Cl, and *p*-CF_3, were prepared by hypochlorite oxidations[8] of known arylamidines.[9] Ultrafast LFP data of these diazirines in ACN, $CHCl_3$, and CHX all give very similar ps transients in the 600−700 nm region; the complete series of spectra in ACN appears in Figures S-4 to S-9 of the Supporting Information. By analogy, we assign these transients to S_1 of **3**; their lifetimes appear in Table 1. Decay curves at λ_{max} for all of the transients can be found in Figures S-1−S-3 of the Supporting Information.

The data in Table 1 show that the S_1 lifetimes of **3** strongly depend on solvent and the aryl substituent. S_1 lifetimes increase with solvent polarity in the order CHX < $CHCl_3$ < ACN, and the lifetimes are enhanced by electron-donating Y substituents regardless of solvent. In fact, we obtain excellent Hammett correlations between τ_2 and σ_p^+, with $\rho = -1.27$ (CHX), −1.37 (ACN), and −1.43 ($CHCl_3$); cf. Figure 2. These are among the very few Hammett correlations of excited state lifetimes.[10] We noted previously that the lifetimes of **1*** (Ar = Ph) increased with the increasing resonance donating ability of X (F > Cl > Br).[2]

We can rationalize the observations with the aid of computational studies. Figure 3 depicts the ground state (S_0) and the first excited state (S_1) geometries of **3** (Y = H), optimized at the RI-CC2/TZVP level of theory.[11] S_1 is not a diradical/zwitterionic species resembling **2**[2] but is instead predicted to be a covalent structure in which the diazirine C−N bonds have lengthened from 1.468 Å in S_0 to 1.546 −1.551 Å in S_1. We also observe bond length alternation in

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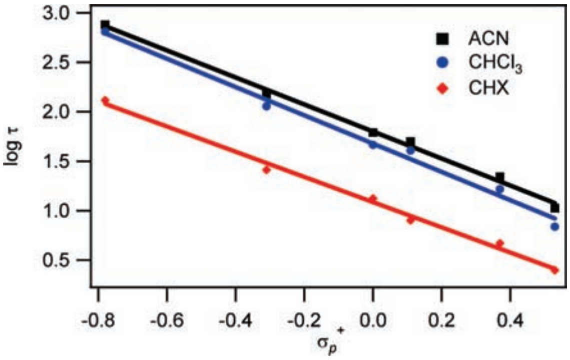

Figure 2. Hammett correlations for S_1 of **3**: log τ vs σ_p^+; see Table 1 for τ and σ_p^+. $\rho = -1.37$ ($r = -0.998$) for ACN (black), $\rho = -1.43$ ($r = -0.995$) for $CHCl_3$ (blue), and $\rho = -1.27$ ($r = -0.996$) for CHX (red).

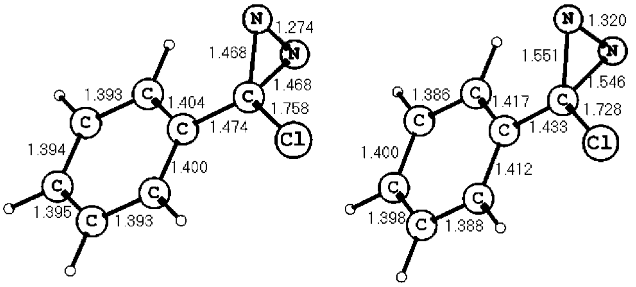

Figure 3. S_0 (left) and S_1 (right) of **3** (Y = H) optimized at the RI-CC2/TZVP level of theory; bond lengths are in Ångstroms.

S_1: the C2−C3 and C5−C6 bonds shorten, while the other C−C bonds lengthen, giving S_1 somewhat of a "quinoidal" appearance, consistent with the charge distribution in S_1 (see below). The S_1 state of the diazirine can either fragment to produce PhCCl and N_2 or relax to the S_0 surface where it can either form the carbene or thermally deactivate. The S_1 or vibrationally excited S_0 states of **3** might also isomerize to the corresponding (unstable) diazo isomer of **3**.

The Mulliken charge distribution[11] in S_1 of **3** (Y = H) indicates that a positive charge resides on the para carbon (+0.04) and on the diazirine carbon (+0.09), while a negative charge accumulates on the nitrogens (−0.12, −0.13) and the ipso carbon (−0.04). Direct interaction of the *p*-Y substituents of **3** with the positively charged para carbon in S_1 accounts for the observed Hammett correlations between τ_2 and σ_p^+.[12] Similarly, resonance donation from X to the positively charged diazirine carbon of **1*** (Ar = Ph) accounts for the previously observed dependence of τ_2 on X.[2]

The RI-CC2/TZVP computed dipole moments of the S_0 and S_1 states of **3** (R = H) are 2.28 and 4.78 D, respectively,[11] which explains why τ_2 of S_1 would be prolonged in polar solvents, as is observed here, where τ_2 tracks solvent polarity (ACN > $CHCl_3$ > CHX). Indeed, for any substituent Y, τ_2 is longest in ACN and shortest in CHX (Table 1). However, solvent polarity has little effect on the Hammett ρ values (see above). This could imply that the main interaction of S_1 with solvent dipoles occurs at the negative (and sterically unencumbered) diazirine nitrogen atoms, rather than at the para carbon, where the positive charge is rather small and the Y substituent might sterically hinder solvation.

In conclusion, experimental and computational studies suggest that 375 nm excitation of arylchlorodiazirines **3** furnishes S_1 excited states with lengthened C−N bonds, a positive charge at the para and diazirine carbon atoms, and a negative charge at the nitrogen atoms. These structures rationalize the observed solvent and substituent effects on the excited state lifetimes.

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Supporting Information Available: Figures S-1−S-9 and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) (a) See the Supporting Information for these calculations. The $S_0 \rightarrow S_2$ vertical transition for **3** (Y = H) is computed at 244 nm (RI-CC2/TZVP) or 302 nm (TD B3LYP/G-311+G(d,p)). (b) Wang, J.; Kubicki, J.; Burdzinski, G.; Hackett, J. C.; Gustafson, T. L.; Hadad, C. M.; Platz, M. S. *J. Org. Chem.* **2007**, *72*, 7581.
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(11) Details of the calculations appear in the Supporting Information.
(12) There is a slight negative charge (−0.01 to−0.02) computed at the meta carbons of the S_1 state of **3** (Y = H), which produces a destabilizing interaction with a *m*-Cl substituent. We include the data for *m*-Cl in the Hammett correlations because we believe that all electrical effects operating between substituents and charges in S_1 contribute to the stability and lifetime of this state.

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